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HETEROGENEITY OF SURFACES

Immersion Calorimetry and Adsorption Studies: Hydrophobic and Hydrophilic Surfaces

and

The Sorption of Water Vapor by Oxide Coated Metals

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Table of Contents

	Page
Abstract	i
Introduction	ii
SECTION I. A THERMISTOR CALORIMETER FOR HEATS OF WETTING; ENTROPIES FROM HEATS OF WETTING AND ADSORPTION DATA	1
Introduction	1
Calorimeter Description	3
Experimental Results and Reproducibility	6
Entropy Calculations: Adsorption of Water on Asbestos	8
SECTION II. ADSORPTION STUDIES ON METALS III. THE SORPTION OF WATER VAPOR ON NICKEL, STEEL AND MOLYBDENUM	12
Introduction	12
Experimental	12
Results and Discussion	15
Metal Powders Activated at Room Temperature	16
Metal Powders Activated at 400°C.	18
Oxide Films on Molybdenum	21
SECTION III. THERMODYNAMICS OF THE ADSORPTION OF WATER ON GRAPHON FROM HEATS OF IMMERSION AND ADSORPTION DATA	23
Introduction	23
Experimental	24
Results and Discussion	25

List of Tables

Page

SECTION I

Table I. Heat of Immersion of Solids in Water at 25° 7

SECTION II

Table I. The Adsorption and Heats of Immersion of Water on Unreduced Metal Powders 17

Table II. Effect of Activation Temperature on the Sorption of Water Vapor by Molybdenum Powder 20

List of Figures

Figure — Following Page No.

SECTION I

1. Heat of Immersion Calorimeter 3

2. Equilibrium and Isosteric Heats of Adsorption for Water Vapor on Asbestos 9

3. Absolute Entropy of Water Adsorbed on Asbestos 9

4. Heats of Immersion for Asbestos in Water Plotted as a Function of Surface Coverage 10

SECTION II

1. Isotherms for the Adsorption of Argon and Water Vapor on Unreduced Molybdenum 16

2. Oxide Films on Molybdenum 21

SECTION III

1. Isotherm for the Adsorption of Water Vapor on Graphon . . 25

2. Heats of Immersion of Graphon in Water Plotted as a Function of Relative Pressure 26

3. Isosteric Heats of Adsorption: Water on Graphon 26

4. Integral and Differential Entropy Curves for Water Adsorbed on Graphon 28

ABSTRACT

I. A heat of immersion calorimeter which employs a thermistor as the temperature sensing element has been constructed to provide data to support our adsorption measurements in studying the heterogeneity of surfaces. Heats of immersion in water have been obtained for asbestos, rutile, Graphon and silica. The thermistor showed excellent sensitivity and stability. The various factors found to influence the reproducibility of the heat measurements are discussed. Heats of immersion were measured for asbestos on which various fractions of a water monolayer had been adsorbed; these heats decreased linearly with surface coverage. This behavior together with the shape of isosteric heat curves was taken as an indication that the surface of asbestos is homogeneous. Absolute entropies of water adsorbed on asbestos were calculated by two methods: 1. from adsorption isotherm data obtained at two temperatures; and 2. from a combination of heats of immersion and single isotherm data. Although the second method gave considerably more precision, both sets of results were in good general agreement.

II. A study of the oxide films present on the surface of nickel, steel and molybdenum was made using both gas adsorption and calorimetric techniques. Nickel and steel powders degassed at 25° were found to exhibit only physical adsorption of water vapor, and the heat of emersion in water was about 550 ergs/cm² for both. Water diffused through the polymolecular film present on molybdenum degassed at 25°, the heat of emersion was 9,500 ergs/cm².

Degassing the nickel powder at 300° removed a strongly bound layer of water and raised the heat of emersion to 950 ergs/cm². After activation of steel at 400°, the equivalent of 10-13 layers of water could be adsorbed indicating the presence of a polymolecular hydrous oxide film. Activation of molybdenum at 400° caused a surprising decrease in the amount of water sorbed per unit area, due probably to the transformation of the porous oxide film to a chemically different, non-porous oxide. Extraction of molybdenum powder with ethyl alcohol removed most of the polymolecular film of oxide from the surface, a hydrous oxide layer, apparently monomolecular, remained.

III. Adsorption isotherms and heats of immersion were measured for the system Graphon-water because Graphon represents a relatively homogeneous surface. The very low adsorption of water by Graphon precluded reliable calculations of thermodynamic quantities from isotherms at two temperatures. Measurements of the heat of immersion as a function of the amount of water pre adsorbed on the Graphon surface in combination with the results obtained from an adsorption isotherm at one temperature allowed the calculation of isosteric heats of adsorption and absolute entropies of the adsorbed state. The isosteric heats of adsorption were much less than the heat of liquefaction and had a minimum value of about 5.5 kcal. near the BET V_m. The thermodynamic criteria of a complete monolayer, the minimum in the S_S curve, corresponded closely to the BET value. This coverage amounted to only 1/1500 of the total Graphon surface area and lends support to the concept of cluster-wise adsorption of water on this surface.

GENERAL INTRODUCTION

A heterogeneous surface is defined as one in which the adsorption sites are not all of equal energy. The distribution of energies may range from the simplest case of two distinct energy groups as postulated, for example, in the Dual Surface Theory of Walker and Zettlemoyer (this Laboratory), to a whole spectrum of energies distributed exponentially among the surface atoms. The heterogeneous nature of the surface may markedly affect its behavior in surface phenomena. For example, slow metallic corrosion would be expected to initiate at the "hot spots" on the surface, i.e., the points of highest adsorption site energy.

Depending upon their origin and in relation to the surface chemistry program in this Laboratory, three distinct types of surface heterogeneity have been distinguished:

1. Physical
2. Chemical
3. Apparent Chemical Heterogeneity

The first type, physical heterogeneity, arises from surface irregularities. From our study of the surface chemistry of molybdenum, the degree of the surface roughness was shown in Technical Report No. 4 to influence not only the strength of interaction with the non-polar gas argon but also to have a marked effect on the fraction of the molybdenum surface which could chemisorb oxygen at low temperatures. Surface roughnes was not a factor in the further studies reported here.

The second type, chemical heterogeneity, arises from the presence of impurities on the surface. There are, of course, many examples of this type, but an especially interesting case is presented by Graphon. This

graphitized carbon black is generally considered to have a quite homogeneous surface; indeed, its behavior toward argon is an almost ideal illustration of homogeneity. Yet, in order to explain the adsorption of water on Graphon it appears necessary to postulate the existence of a very small amount of surface heterogeneity caused by traces of chemisorbed oxygen. Thus, Graphon possesses a particularly well-defined surface for elucidating the nature of chemical heterogeneity. In addition, it is representative of hydrophobic surfaces and, therefore, adsorption results on it are of interest in fields such as protective coatings. For these reasons, one phase of the present work has been directed toward a study of the Graphon-water system.

The third type, apparent chemical heterogeneity, may be actually produced by a completely homogeneous surface. This behavior is illustrated by evaporated molybdenum films and sintered molybdenum powder, as discussed in Technical Report No. 4, and is the basis for the third classification of surface heterogeneity. In this case, the adsorption of molecules or atoms on the surface changes the energies of the neighboring surface sites. This effect is particularly marked in the chemisorption of gases on a reduced metal where the adsorbed atoms may lower the work function of the metal to such an extent that the process stops after only a fraction of the surface has reacted. Thus, even a homogeneous, single crystal of a metal may appear to have a heterogeneous surface.

Previous reports in this series have shown how thermodynamic quantities such as isosteric heats of adsorption and absolute entropies of the adsorbed state are valuable in characterizing the heterogeneity of a surface. A rapid fall in the isosteric heats of adsorption in the region

below monolayer coverage is generally considered a criterion of a heterogeneous surface, whereas an initial constant value followed by a marked rise in the curve near V_m denotes a homogeneous surface. The shape of the absolute entropy curve, while generally not as easily interpreted, is also indicative of the uniformity of the surface.

In order to support the thermodynamic results obtained from gas adsorption data, another experimental approach was deemed necessary. Therefore, a thermistor calorimeter designed to measure heats of immersion was constructed. This apparatus not only increases the precision with which thermodynamic data can be obtained but also greatly widens the range of systems that can be studied. The study of the properties of oxide films on different metals given in Section II of this report illustrates the value of heat of immersion measurements in obtaining a quantitative measure of the porosity and hydrous nature of oxide coatings. More strikingly, the increased precision obtained by combining the two types of data, adsorption and calorimetric, is shown in the studies of a quite homogeneous surface, asbestos, and a heterogeneous surface, Graphon, in so far as water adsorption is concerned. It is of interest that without the immersion calorimeter no thermodynamic data could have been obtained for the system water-Graphon; these results, incidentally, represent the first calculations made from a combination of such experimental data. For asbestos, the linearity of the heat of immersion curve with increasing amounts of water pre-adsorbed on the surface provides striking confirmation of the surface homogeneity of this substance.

The present report, then contains four sections, the first three covering the various phases of the project (in manuscript form):

I. A description of the immersion calorimeter and its application in the study of the homogeneous surface, asbestos; II. The results of the investigation of the properties of metal oxide films; III. A study of the system water-Graphon. The last section contains a summary of current work. For convenience the references are numbered separately in each section.

A THERMISTOR CALORIMETER FOR HEATS OF WETTING; ENTROPIES FROM HEATS OF WETTING AND ADSORPTION DATA *

INTRODUCTION

In order to provide further information on the interaction between surfaces and adsorbates supplemental to that obtained from gas adsorption measurements, heats of immersion were desired. For such measurements there is a need for a convenient and relatively inexpensive calorimeter free from inherent errors. The small amount of heat liberated by immersion of a solid requires a detector of a high order of sensitivity. Hutchinson[1]

(1) E. Hutchinson, Trans. Faraday Soc., 43, 443 (1947).

has reported on the use of a thermistor in immersion calorimetry but gave no data on either the sensitivity or stability. In recent cryoscopic work in this Laboratory[2] thermistors were shown to have both high sensi-

(2) R. R. Myers, Ph.D. Thesis, Lehigh University, 1952.

tivity and good stability; this work suggested a detailed investigation of their use in calorimetry. The performance of a calorimeter utilizing a thermistor as a temperature sensitive element has been tested and found entirely satisfactory for the measurement of heats of immersion.

Recently, Jura and Hill[3] have pointed out that theoretically

(3) G. Jura and T. L. Hill, J. Am. Chem. Soc. 74, 1598 (1952).

the absolute entropies of adsorbed molecules can be obtained from a combination of heats of immersion with spreading pressures from a single

* This article has been preprinted in the J. of Phys. Chem., 27th National Colloid Symposium, June 25-27, 1953. pp. 43-46.

isotherm with considerably more accuracy than entropy calculations dependent on the difference in spreading pressures obtained at two temperatures. It was pertinent to inquire, then, whether the calorimetric approach was experimentally capable of yielding data of sufficient precision to permit accurate evaluation of entropies from heats of immersion. An additional purpose of this investigation was to compare the results determined by this method with values obtained from isothermal data alone. Because of extensive adsorption studies on asbestos underway in this Laboratory, the asbestos-water system was chosen for this comparison.

Part I. A THERMISTOR CALORIMETER FOR HEATS OF WETTING

The Calorimeter. - The calorimeter used to measure heats of wetting, Fig. 1, consisted of a wide-mouth, silvered Dewar flask cemented to a Plexiglas ring to which the Plexiglas top could be bolted when assembled. The apparatus was fitted with a vacuum seal stirrer, A; a small heating coil, B, of 5 ohms resistance for calibration; and the thermistor, C.[4] The sample tube was held firmly in the sample holder, D, and broken

(4) The thermistor, 15A, was supplied by the Western Electric Co., Allentown, Pennsylvania.

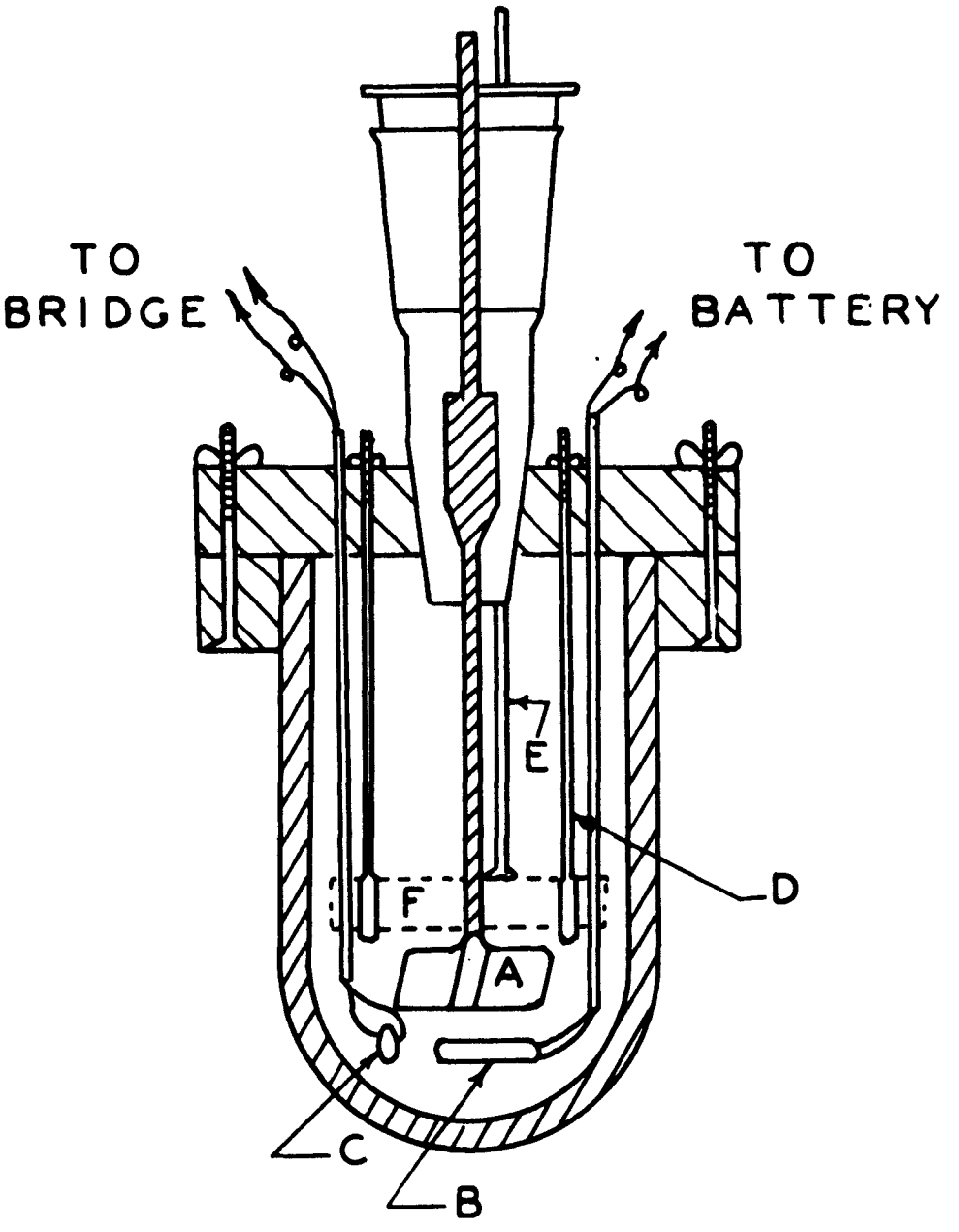
by tapping the steel rod, E, resting on top of the sample tube, F.

The apparatus was housed in a specially constructed constant temperature air-bath except for the stirrer and breaker rod which extended through the top of the bath. The walls of the bath were two inches thick and consisted of alternate layers of sheet cork and aluminum foil separated by air pockets. The temperature was controlled by a cooling coil and a 100-watt heater operated by a micro merc-to-merc thermoregulator and thyratron relay. Air circulation in the bath was produced by a 10-inch bucket-blade propeller turning at 1750 r.p.m. The temperature variation in the air bath was less than $\pm 0.005°$.

As pointed out by Boyd and Harkins,[5] the following factors were

(5) G. E. Boyd and W. D. Harkins, J. Am. Chem. Soc., 64, 1190 (1942).

of primary importance in developing the calorimeter: type and rate of stirring; high accuracy of the measurement of temperature changes; accurate determination of the electrical energy equivalent; and rapid attainment of thermal equilibrium with the calorimeter. In addition, the attainment



CALORIMETER
FIGURE I

of a suitable rating period before breaking the sample tube and the stability of the thermistor were also found to be important considerations.

Stirring. - A desired rate of stirring was predetermined by observing the dispersion of samples of various particle size and density. A stirring rate of 150 r.p.m. gave optimum dispersion and a minimum heating effect. To aid in the complete wetting of the powders only 3- to 8-g. samples were used in 350 ml. of water.

Temperature Measurement. - The comparatively small temperature increases accompanying the wetting of a solid amounted to about 0.01° for most of the samples used in the calorimeter. These temperature changes were followed by measuring the change in resistance of the thermistor by means of a Mueller resistance bridge (Eppley Co., No. 301). At 25° the thermistor had a resistance of approximately 103 ohms and a temperature coefficient of approximately 5 ohms per degree. The Mueller bridge, used in conjunction with a Leeds and Northrup Type HS galvanometer, was found capable of detecting changes of resistance of 0.0001 ohm.

Rating Period. - The slopes of the temperature or resistance versus time plots were found to influence greatly the accuracy of the determination of temperature increases. Therefore, these slopes were made small enough so that the smallest changes of temperature detectable on the Mueller bridge could be measured easily. Thus, for example, it was possible to measure temperature changes of 0.00002° (0.0001 ohm) if this change took place over a 20 to 60 second period.

When the air-bath and calorimeter were at the same temperature, the heat evolved due to stirring gave a rating period with a slope of

about 0.0070 ohm per minute. A suitable initial rating period was obtained by the simple expedient of heating the calorimeter contents until a temperature differential of about 0.4° was established between the calorimeter and the bath. The rating period thus obtained had a slope of about 0.0001 to 0.0005 ohm per minute. The curve was found to be linear during the 5 to 10 minute rating period. The heat of immersion usually raised the temperature about 0.01°, an amount which did not materially affect the final rating period.

Sample Tube Breaking. - The sample tubes were made of specially constructed, thin wall glass tubing. In initial experiments, tubes were broken by screwing down a steel rod, but it was found that some heat was evolved from the friction of the rod against the sample bulb; although small, this heat could be practically eliminated by shattering the bulb by tapping the breaker rod lightly. Blank runs indicated that the heat effect resulting from breaking in this fashion was so small that it contributed only from 0.2 to 0.4 joule to the total heat. A correction of 0.3 joule was applied to all measurements.

Calorimeter Calibration. - Calibrations were carried out by comparing the temperature change due to immersion of powders to the temperature change caused by a known amount of electrical energy introduced by the heater. A calibration was carried out after each run. In the small temperature range studied a linear relationship[6] was found between

(6) Over large temperature ranges a linear relationship exists between ln R and 1/T.

the change in resistance, ΔR, of the thermistor and the electrical energy input, ΔQ. The stability of the thermistor was entirely satisfactory; over a three-month period the $\Delta R/\Delta Q$ slope remained constant at 0.00246 ± 0.00003 ohm/joule.

Procedure. - The samples were evacuated at 400° for 4.0 hours before heats of immersion were obtained, then were sealed off under vacuum and transferred to the sample holder. Exactly 350 ml. of distilled water at a temperature below 25° was added to the Dewar flask. Stirring was begun and bath and calorimeter were allowed to reach temperature equilibrium. The temperature of the calorimeter was raised slightly above the bath temperature by means of the heating coil. A time-resistance curve was then followed until a steady change in resistance was observed for a 6-minute rating period. The slope of this initial curve was not allowed to exceed 0.0001-0.0005 ohm per minute. Then the sample was broken under the liquid and the time noted. Time-resistance readings were continued for 5-10 minutes after breaking. The heat of wetting was always evolved within one or two minutes after breaking.

Experimental Results and Reproducibility. - In Table I values of the heats of immersion for a variety of powders are given. The breaking errors were computed for the smallest amount of a particular sample used and, thus, are maximum values. The average deviations represent a measure of the reproducibility of the results. However, a combination of factors such as weighing, pretreatment, activation and evacuation of the samples as well as calorimetric behavior affect these values.

Table I

HEAT OF IMMERSION OF SOLIDS[a] IN WATER AT 25°

Sample	Specific area,[b] m.²/g.	Heat of immersion, ergs/cm.²	Av. deviation ergs/cm.²	Minimum heat evolved, joules	Maximum error due to heat of breaking, %
Asbestos[c]	20.0	850	± 20	30.0	0.3
Graphon[d]	83.0	51	± 6	7.5	1.3
Rutile[e]	7.3	550	± 18	18.0	0.6
Silica[f]	0.96	564	± 16	4.0	2.5

[a]Solids evacuated at 400° for 4.0 hours. [b]All areas determined from nitrogen adsorption data except asbestos for which water adsorption data were used. [c]7-R fiber, Canadian Johns-Manville Company. [d]Furnished by Godfrey L. Cabot Company. [e]Titanium pure R-300, du Pont Company. [f]New Jersey Silica Sand Company.

The immersional heat values found for silica and rutile differ by 16 and 30 ergs/cm.², respectively, from the values found for these materials by Harkins.[5] Since the purity and history of the samples undoubtedly differ, this represents good agreement. The low heat value found with graphon is not surprising since graphon is a hydrophobic solid which exhibits a large contact angle with water.

Part II. ENTROPIES FROM HEATS OF WETTING AND ADSORPTION DATA

Water Vapor Adsorption Measurements. - The apparatus employed for water vapor adsorption measurements in this research was similar to the type described by Orr[7] except for the following changes: (1) Apiezon B

(7) Orr, Proc. Roy. Soc. London, 173A, 347 (1939).

was used in the manometers since this oil was found not to absorb water vapor; (2) absolute adsorption pressures were measured rather than differential pressures. A cathetometer was used for reading low pressures on the oil manometer. The limit of sensitivity was 0.004 mm. Hg., however, considerable scatter in the data was found below pressures of 0.09 mm. The dead space volumes were calibrated with helium. Blank runs determined that adsorption of water by the apparatus was negligible.

The asbestos samples were evacuated at 25° for 12 hours at 10^{-5} mm. before adsorption measurements were taken. These conditions were chosen since it was desired to remove only the physically adsorbed water from the surface of asbestos. An increase of the evacuation temperature to 425° was found to be necessary before the more tightly bound water could be completely removed.[8]

(8) A comprehensive discussion of adsorption by asbestos is to be published later.

Heats of Adsorption and Entropy of the Adsorbed State from Isothermal Data. - The isosteric heats of adsorption, $H_G - \bar{H}_S$, and equilibrium heats of adsorption, $H_G - H_S$, with the corresponding entropy values, $S_G - S_S$, were calculated for the adsorption of water vapor on

asbestos. The isosteric heat values were calculated in the usual manner from the Clausius-Clapeyron equation at constant volume adsorbed. The equilibrium heats of adsorption were obtained[9] from the Clausius-Clapeyron

(9) The symbols and method of calculations correspond to those indicated by Hill, J. Am. Chem. Soc., 17, 520 (1949).

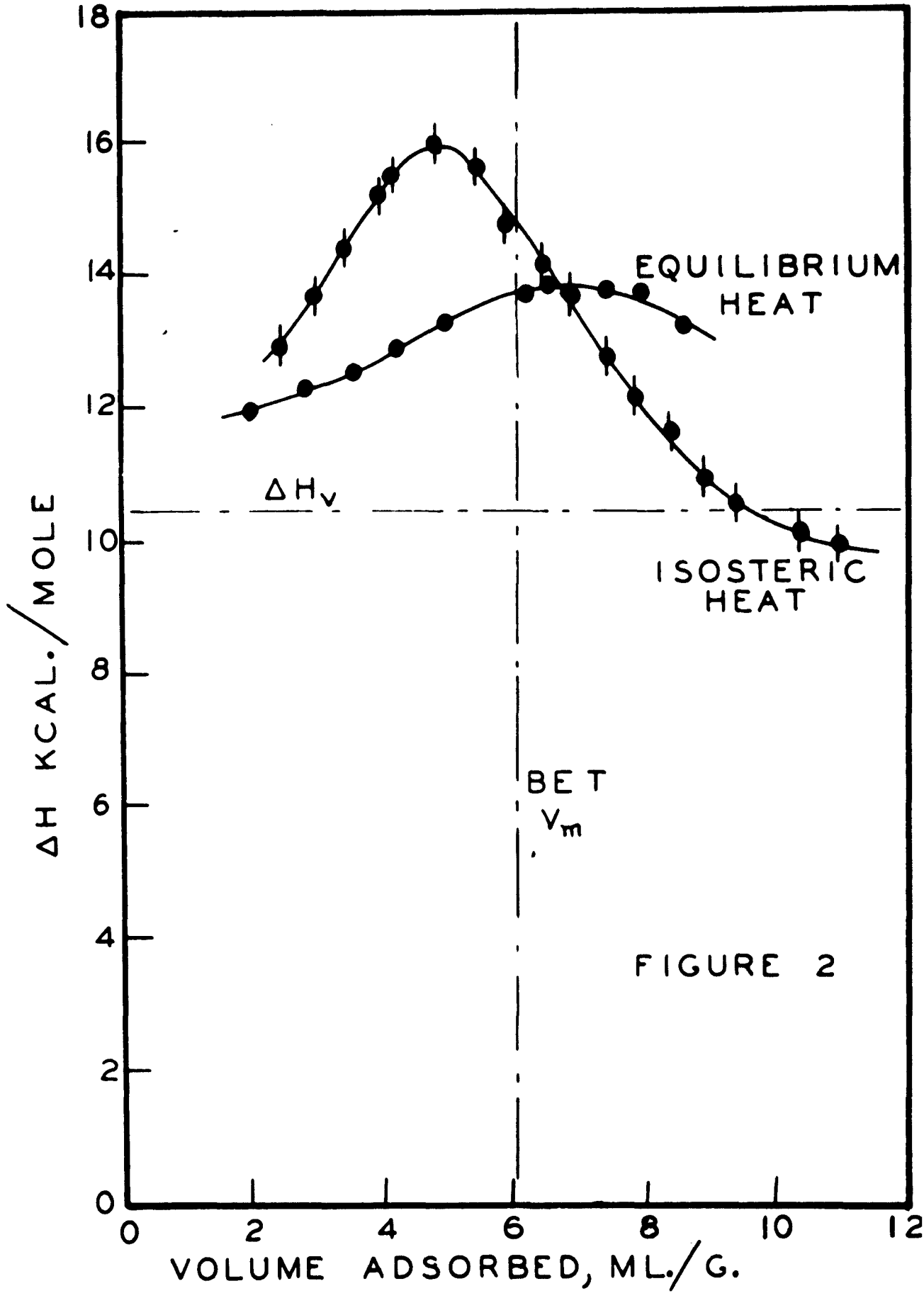
equation at constant spreading pressure, φ. Thus, it was necessary to determine the spreading pressure as a function of the equilibrium pressure at two temperatures from isothermal data either by graphical integration of the Gibbs equation

$$\varphi = kT \int_0^p \Gamma \, d \ln p$$

where Γ is the surface concentration, or by integration of a plot of V/p vs. p. Integrations of both V vs. ln p and V/p vs. p plots were carried out graphically by use of a polar planimeter. Although spreading pressures obtained by integration of either plot agreed quite closely, the plot of V vs. ln p could be extrapolated to zero coverage with more reliability.

The equilibrium and the isosteric heats of adsorption for water vapor on asbestos are presented in Fig. 2 and are indicative of adsorption on a homogeneous surface.

The entropy terms, $S_G - S_S$, were evaluated from the equilibrium heats of adsorption by the relation $S_G - S_S = (H_G - H_S)/T$. The entropy of water vapor, S_G, was calculated at the various equilibrium pressures and the absolute entropy of the adsorbed state, S_S, plotted in Fig. 3, was determined as a function of volume adsorbed.



ISOSTERIC AND EQUILIBRIUM HEATS OF ADSORPTION
FOR WATER ON ASBESTOS AT 25°C.

INTEGRAL ENTROPY OF ADSORBED WATER
ON ASBESTOS AT 25°C.

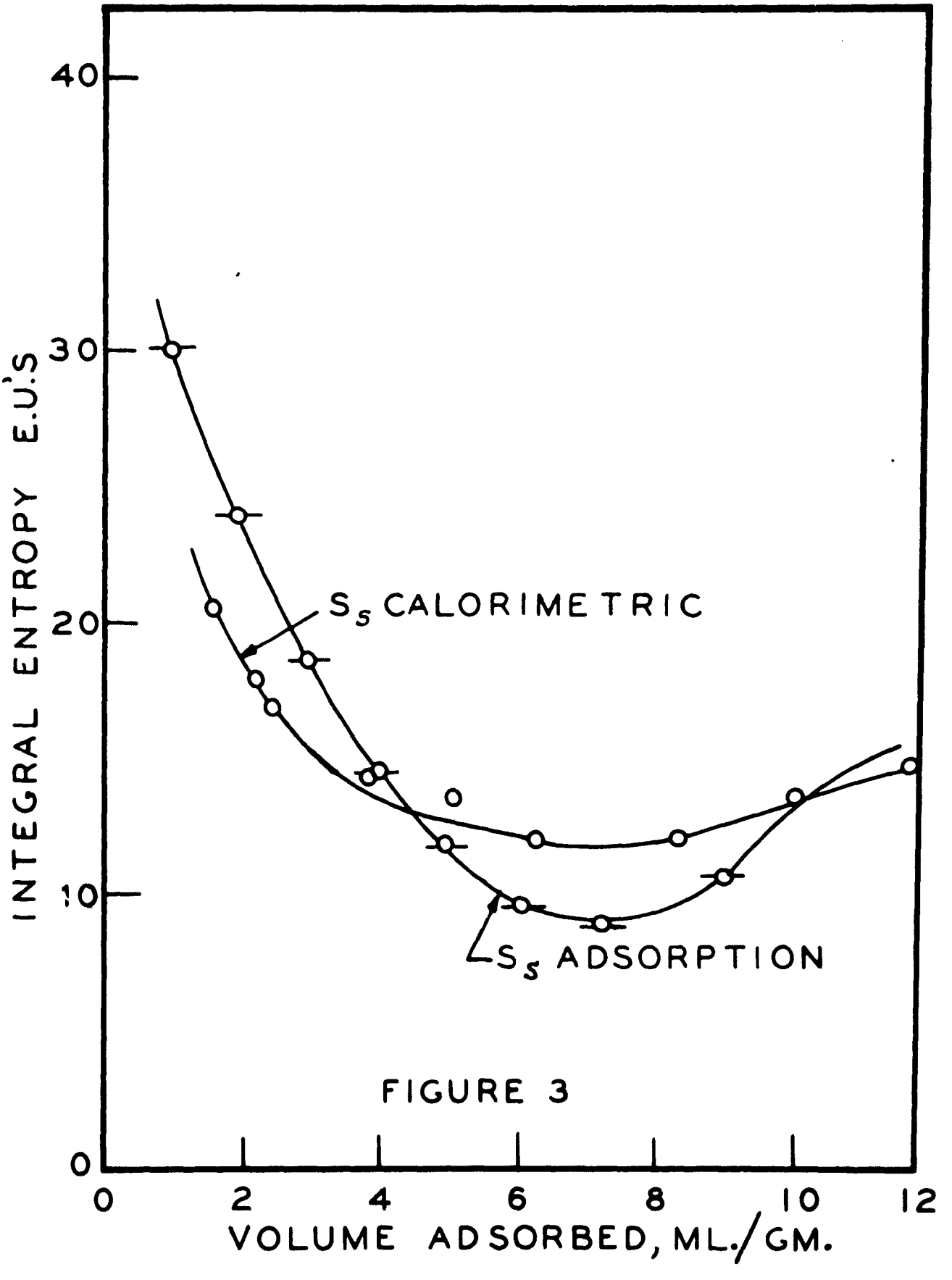


FIGURE 3

Entropy of the Adsorbed State from Heats of Wetting. - The entropy of the adsorbed state was also calculated independently from the equation

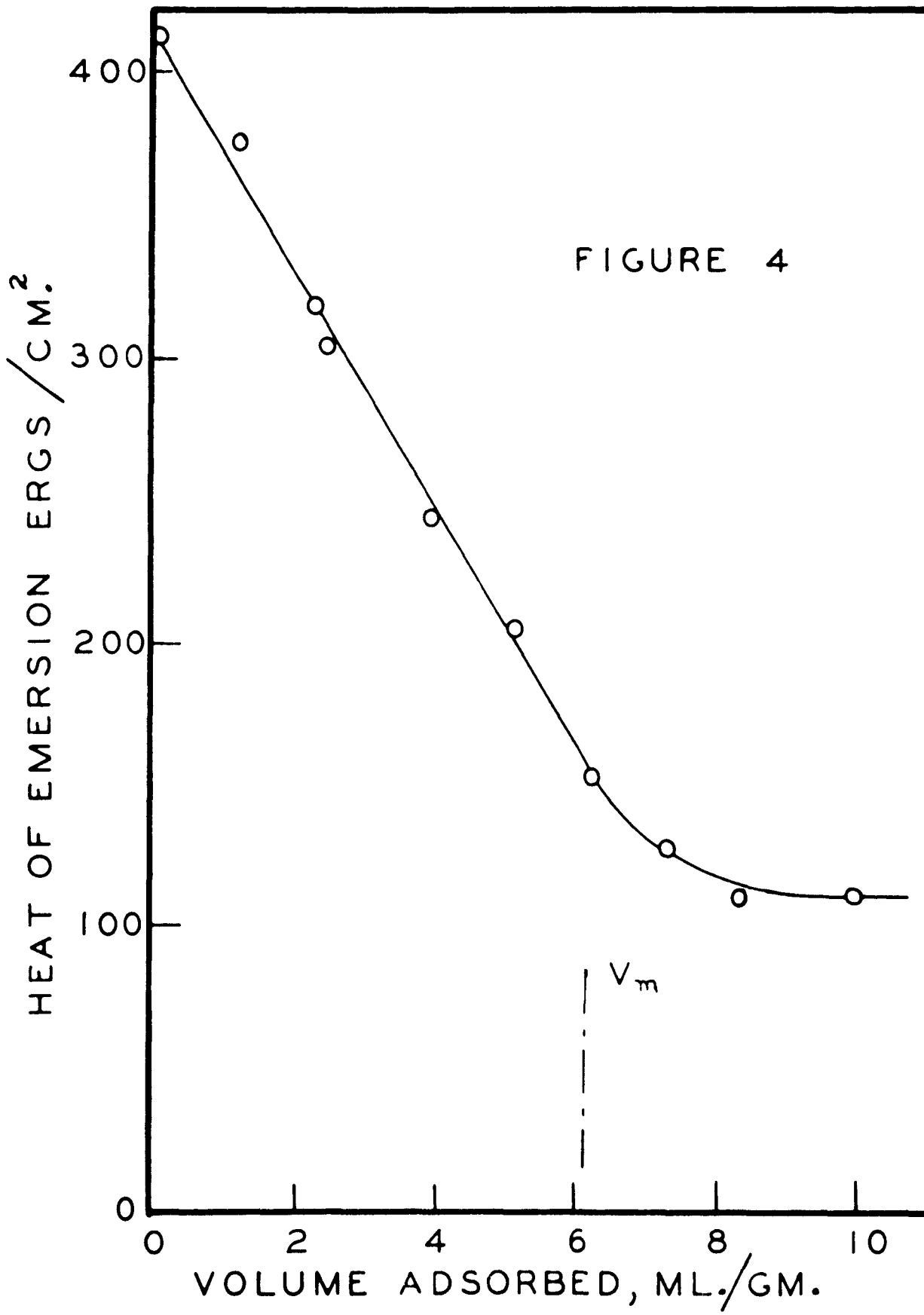
$$T(S_S - S_L) = \frac{U - U_o}{N_S} + \varphi/\Gamma - kT \ln x \qquad (1)$$

as developed by Jura and Hill.[3] In this equation S_L refers to the entropy of the liquid adsorbate (in equilibrium with vapor), $U - U_o$ is the difference in the heat of wetting between the clean solid, U_o, and the film coated solid, U, and x is the relative equilibrium pressure of the film coated solid.

The film coated asbestos samples were prepared on the adsorption apparatus and sealed off at the desired equilibrium pressure. Care was taken to ensure that the temperature of the sample was not altered during the cutting-off operation. Values for the heats of wetting for evacuated asbestos and for the film-covered asbestos at various coverages are presented in Fig. 4. The linear relation between the heat of wetting and volume adsorbed up to about monolayer coverage is notable and was taken to be indicative of surface homogeneity since the heat evolved on wetting is dependent only on the energy of particular parts of the surface; the energy of the adsorption sites is constant. The heat of wetting measurements thus support the conclusions of surface homogeneity drawn from the isosteric and equilibrium heat of adsorption curves.

The term $T(S_S - S_L)$ was calculated from equation 1 and the entropy of the adsorbed state, S_S, was evaluated. The entropy of the adsorbed state as a function of volume of water vapor adsorbed is also presented in Fig. 3 in comparison with the entropy curves as determined from the equilibrium heat values.

HEATS OF EMERSION OF ASBESTOS
FROM WATER AT 25°C.



Comparison of Methods. - Figure 3 contains the entropy curves obtained from calculations based on both calorimetric and adsorption data. The agreement obtained is remarkably good despite the larger errors inherent in calculations from adsorption data. The errors in these entropy values were computed from the equation of Hill and Jura[3]

$$S'_S - S_S = \frac{1}{\Gamma}\frac{\Delta a}{\Delta T}$$

where S'_S and S_S are the apparent and true entropy values and Δa is the error in the spreading pressures. The estimated maximum error in entropy varied from over 100% at low pressures to about 20% at monolayer coverage. In computing the error in entropy values obtained from calorimetric data, errors from the following sources were considered: (1) errors in the determination of φ; (2) errors in the determination of $(U - U_0)/N_S$; (3) errors in determining the relative pressure. Errors in entropy values obtained from calorimetric data were found to range from ca. 35% at low coverage to 8% at monolayer coverage. Thus it is apparent that comsiderably more reliance can be placed on the entropy values obtained from the latter method.

Acknowledgment. - The authors gratefully acknowledge the financial support provided by the Office of Naval Research, Project NR 057-186, Contract N8onr-74300. We also wish to thank Miss Yung-fang Yu for assistance in obtaining some of the adsorption data.

ADSORPTION STUDIES ON METALS III. THE SORPTION OF WATER VAPOR ON NICKEL, STEEL AND MOLYBDENUM

INTRODUCTION

The importance of oxide films on metals in such fields as corrosion, lubrication and adhesion has long been recognized. For this reason, a detailed knowledge of the physical and chemical properties of such films is important. To this end, the techniques of adsorption and calorimetric measurements were utilized to provide information concerning the hydrous nature, molecular thickness, porosity, and stability of oxide films on a variety of metals.

EXPERIMENTAL

Materials. - The molybdenum powder[1] was prepared by the

(1) All samples were furnished by Dr. Norman Hackerman of the University of Texas.

Westinghouse Electric Company, Bloomfield, New Jersey by high temperature reduction of the oxide. The purity of the freshly prepared sample was reported to be greater than 99.9 %. The nickel powder was prepared by the International Nickel Company, Inc., New York, by high temperature reduction of the carbonyl and was of very high purity. The SAE 1020 steel powders were furnished by the Exomet Corp., Conneaut, Ohio. The steel had been atomized at a maximum temperature of 1620°C. and annealed at a temperature of about 1000° under hydrogen cover with a small amount of propane present to prevent carbonization. Since the droplets formed during

atomization were molten the resultant particles had a relatively smooth surface and the metal in this form should possess properties characteristic of some practical steel surfaces. The steel had the following percent composition: C, 0.25; Si, 0.15; Mn, 0.34; S, 0.007; and P, 0.012.

High purity tank argon and helium were used in the adsorption measurements. The argon was further purified by passage through fine copper gauze heated to 500° and dried with anhydrous calcium sulfate. The helium used in dead space determinations was purified by passing it slowly through a charcoal trap immersed in liquid nitrogen. Distilled water was evacuated for long periods of time before use to remove dissolved gases.

Pretreatment of Surfaces. - Adsorption and heat of wetting measurements were determined on all the unreduced samples. These powders had been subjected to no treatment after manufacture except storage under normal atmospheric conditions long enough for an oxide film to have developed on their surfaces. Before use these samples were degreased with benzene and degassed under high vacuum either at 25° for 24.0 hours or at 400° for 3.0 hours.

Since the molybdenum metal was known[2] to possess a polymolecular

(2) F. H. Healey, J. J. Chessick and A. C. Zettlemoyer, J. Phys. Chem. 57, 178 (1953).

surface film of the complex oxide molybdenum blue, $MoO_2 \cdot 4\ MoO_3 \cdot x\ H_2O$, additional samples of this metal were further pretreated by extracting with ethyl alcohol in a Soxhlet apparatus. The oxide is soluble in alcohol and the treatment was continued until no further blue coloration was imparted to the liquid. The molybdenum powder was then transferred

to a suitable bulb while still wet and evacuated at 400° to remove adsorbed alcohol. This treatment removes most of the oxide film from the metal--probably all except the monomolecular film in contact with surface metal atoms. Molybdenum samples treated in this manner were used in the adsorption and heat of wetting measurements in addition to molybdenum which had only been degreased with benzene.

The difficulties generally encountered in the preparation of metal powders with large surface areas are well known. Therefore, it is interesting to note that alternate soxhleting of molybdenum powder with alcohol and reoxidation with moist oxygen can be utilized as a method for the preparation of high area samples of molybdenum.

Apparatus and Procedure. - The adsorption measurements were determined in an apparatus described by Orr[3]. However, in this work

(3) W. J. C. Orr, Proc. Royal Soc. London 173A, 349 (1939).

absolute pressures were measured rather than differential pressures. An oil manometer allowed adsorption pressures in the range 0.10 to 50.0 mm. of mercury to be measured. Apiezon "B" was used in the manometer. This oil has a very low vapor pressure and did not dissolve any of the gases used. Blank determinations showed that the volume of water vapor adsorbed on the walls of the glass sample system at 25°C. was negligible in comparison to that volume absorbed by the sample in the relative pressure region from zero to 0.4.

Argon was adsorbed on the samples at -195°; water vapor at 20°C. Specific areas of the samples were calculated using the usual BET method.

The calorimeter used in the heats of wetting measurements has been fully described.[4] A thermistor was used to measure temperature changes.

(4) A. C. Zettlemoyer, G. J. Young, J. J. Chessick and F. H. Healey. To be published in the J. of Phys. Chem., October 1953.

RESULTS AND DISCUSSION

The results of the adsorption and heat of wetting measurements on the unreduced metal powders are summarized in Table I. The specific surface areas in column two were obtained from argon adsorption data. To illustrate the differences in the water vapor sorption by the various powders activated at different temperatures the V_m values which generally represent the STP volumes of gas required to cover the surface of one gram of powder with one layer, were obtained from water adsorption data by the BET method[5]. These calculated V_m values, however, may include not

(5) S. Brunauer, P. H. Emmett and E. Teller, J. Am. Chem. Soc. 60, 309 (1938).

only this monomolecular volume of gas, but also water sorbed into the porous oxide layer, and/or water irreversibly sorbed on the surface, i.e., water which cannot be removed by evacuation at 20°, the temperature of the adsorption run. These V_m values were arbitrarily converted for the purpose of comparison into an amount equivalent to the number of layers of water molecules which could be accommodated on the external surface of the powders as measured by the argon adsorption data[6]. A typical set of

(6) The V'm values for both argon and water vapor were converted into specific areas by use of the proper factors. The equivalent number of water layers was then obtained by dividing the water surface area by the argon surface area.

isotherms for the adsorption of argon and water vapor on an unreduced metal powder is shown in Figure 1.

The area occupied by a single adsorbate molecule was calculated on the basis of hexagonal close packing. The cross-sectional areas used were 13.9 $Å^2$ and 10.8 $Å^2$ for argon and water respectively.

Studies on Metal Powders Activated at Room Temperature. It is evident from Table I that the adsorption of water vapor by nickel and steel powders degassed at 25° differs markedly from that by molybdenum studied under similar conditions. Good agreement was found between areas calculated from both argon and water vapor adsorption data for the first two powders; water vapor was only physically adsorbed on their external surfaces. On the other hand the original molybdenum sorbed about eight times more water than could be accounted for on the basis of external area alone. Diffusion of water molecules through the polymolecular, porous-oxide film of molybdenum blue present on the surface of the powder accounts for the high sorption of water. Evidently this water of hydration forms a weak enough bond with oxide molecules so that it can be readily removed by evacuation at room temperature.

The heat of emersion of nickel degassed at 25° was determined to be 590 ergs/cm^2; this is a reasonable value for the wetting of a non-porous oxide which physically adsorbs water on its surface[7]. The heat

(7) W. D. Harkins, The Physical Chemistry of Surface Films, Reinhold Publishing Co., New York, N. Y., 1952, p. 264.

of emersion value determined for steel degassed at 25°, about 500 ergs/cm^2

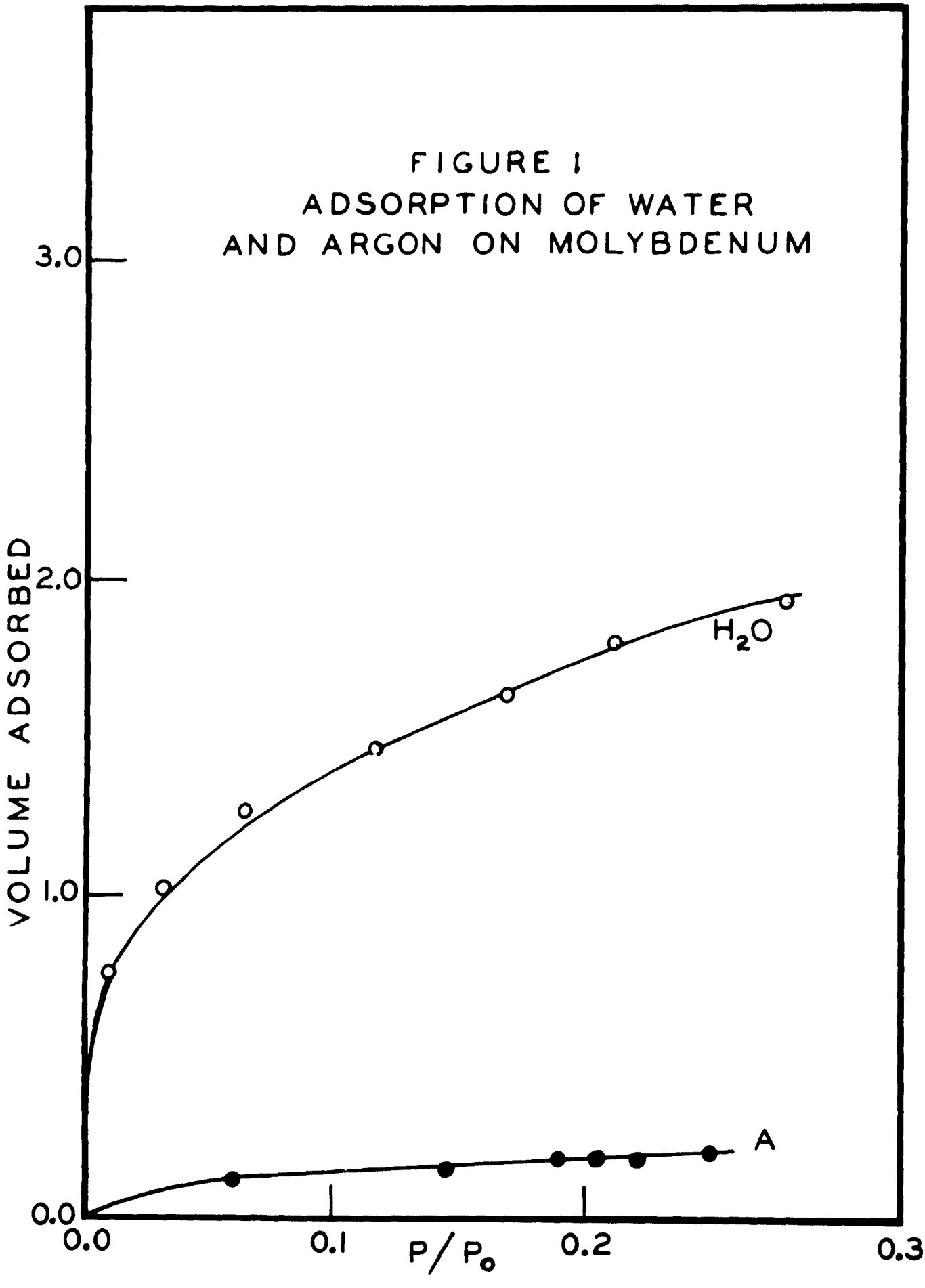


FIGURE 1
ADSORPTION OF WATER
AND ARGON ON MOLYBDENUM
VOLUME ADSORBED
3.0
2.0
1.0
0.0
0.0
0.1
0.2
0.3
P/P₀
H₂O
A

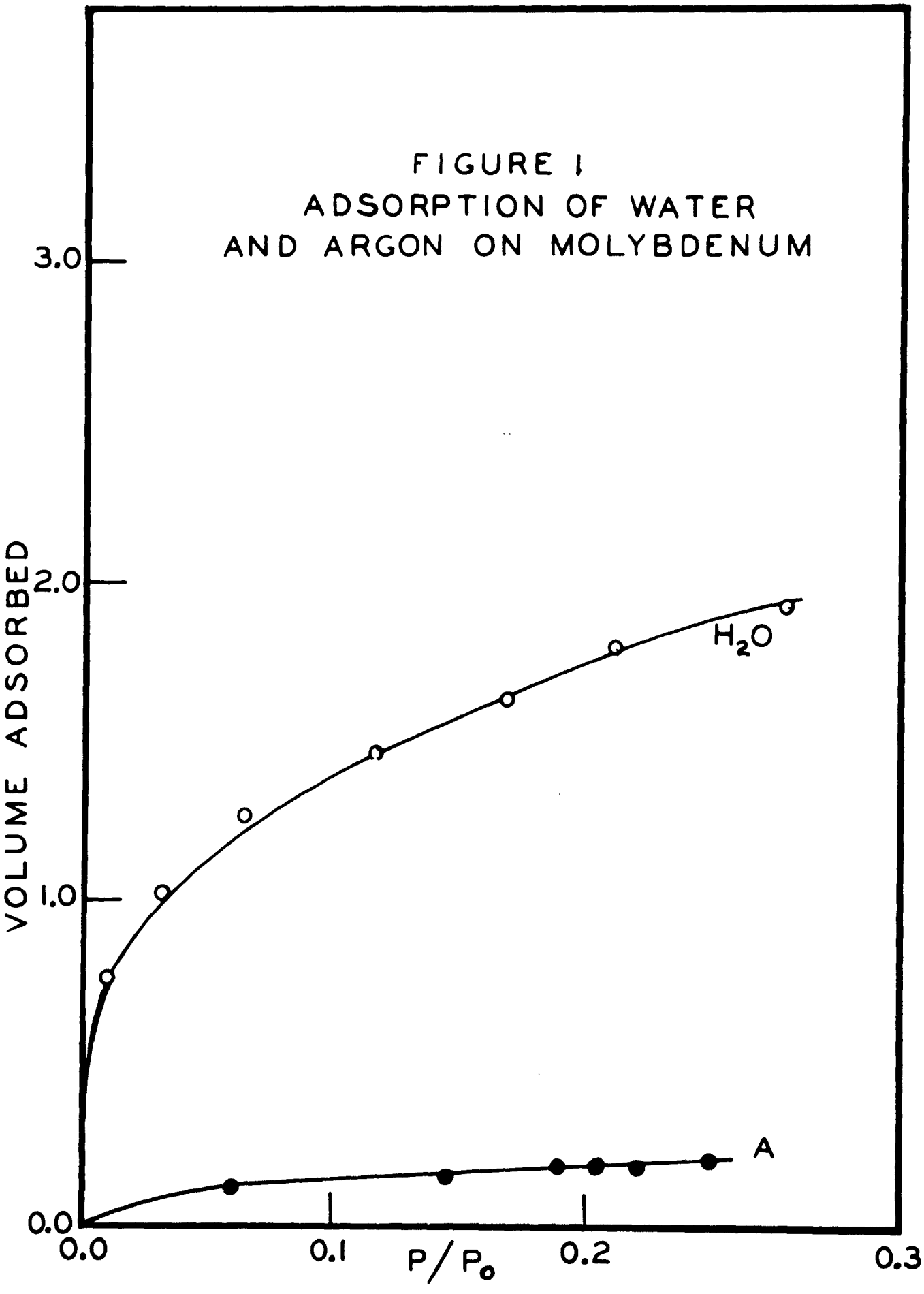


FIGURE 1
ADSORPTION OF WATER
AND ARGON ON MOLYBDENUM
VOLUME ADSORBED
3.0
2.0
1.0
0.0
0.0
0.1
0.2
0.3
P/P₀
H₂O
A

Table I

The Adsorption and Heat of Emersion of Water on Unreduced Metal Powders

Powder	Activation Time Hrs.	Activation Temp. °C.	Surface Area $m^2/g.$	Calc. No. of Water Layers	Heat of Emersion $ergs/cm^2$
Nickel	24.0	25	0.68	1.1	590
	3.0	300	0.74	1.9	953
Steel	24.0	25	0.16	0.9	500
	3.0	400	0.08	10 to 13	
Molybdenum	24.0	25	0.55	7.9	9,510
	3.0	400	0.91	0.9	
Molybdenum[a] (Sintered)	24.0	25	0.38	5.1	4,750
	3.0	400	0.69	1.0	
		Samples Soxhleted with Alcohol			
Molybdenum	3.0	400	0.97	4.4	5,502
Molybdenum[a]	3.0	400	0.49	4.1	5,050

(a) Sintered samples had been reduced repeatedly at elevated temperatures. They were then stored for long periods of time (in the presence of air) before use at 25°.

was the same order of magnitude as that for nickel.[8] For the original

(8) Unfortunately, the surface area of steel powder activated at room temperature was too small to allow the accurate determination of heat of emersion values with the present calorimeter.

sample of molybdenum, however, the heat value was found to be 9,510 ergs/cm^2, or about 1,200 ergs/cm^2 per water layer. This high value suggests that water diffuses into the surface oxide layer on molybdenum and forms a hydrogen bond with an oxide molecule.

The amount of complex oxide removed from the surface of molybdenum powder by extraction with alcohol amounted to 1.03% of the total weight of powder. If it is assumed that one layer of water is physically adsorbed on the surface of the oxide, and further that the stoichiometric formula of the oxide is given by the following, $MoO_2 \cdot 4MoO_3 \cdot 4H_2O$, then the ratio of the moles of water of hydration per mole oxide amounts to 4.2. The average heat of hydration has been calculated to be 19,800 calories per mole of water.

Metal Powders Activated at 400°C. - After activation at 400°, the calculated number of water layers sorbed on a nickel surface was found to be approximately two, an amount almost double that for a sample of nickel activated at 25°. The heat of emersion increased from 590 to 953 ergs/cm^2. These results support the statement of Tingle[9] that the surface

(9) E. E. Tingle, Trans. Faraday Soc., 46, 43 (1950).

of nickel is covered with a tough, compact film of oxide impervious to water. This film, however, adsorbs a monomolecular film of water strongly enough so that is resists removal by room temperature evacuation at 10^{-5}mm. Hg.

The steel samples activated at 400° sorbed large quantities of water vapor; an amount equivalent to 10-12 surface layers of water. Evidently, these powders also have a polymolecular, hydrous oxide on their surface. However, unlike molybdenum, the water sorbed into the interior of the oxide layer is bound strongly enough to the metal oxide sites to resist removal by evacuation at low temperatures.

Because of the polymolecular, hydrous oxide film on the surface of molybdenum, it was presumed that high temperature activation of these powders would lead to an increased sorption of water vapor. Surprisingly, the uptake of water was found to decrease with increasing activation temperature. It is evident from an inspection of Table II that the specific area of the powder, as calculated from argon adsorption data, about doubled as the activation temperature increased from 25° to 400°, whereas the calculated number of water layers decreased eight fold. Further, good agreement was found between areas calculated from both argon and water adsorption data after the 400° activation. Apparently water was only physically adsorbed on the exposed surface of the molybdenum. There is no doubt that high temperature activation of molybdenum causes profound changes in the oxide structure present on its surface. Transformation of the complex oxide "molybdenum blue" initially present into a more dense, non-porous but rougher oxide layer would account for the increase in specific area as well as the decrease in water uptake.

To check the belief that the surface oxide was changed chemically by activation at elevated temperature, a pure sample of the complex oxide "molybdenum blue", which had been dissolved from a large sample of

molybdenum powder by soxhleting with ethyl alcohol, was heated to 350°. The blue oxide changed to a more dense, grayish mass which no longer dissolved in water or alcohol. The composition of the new oxide was not determined.

Table II

Effect of Activation Temperature on the Sorption of Water Vapor by Molybdenum Powder (Original Sample)

Argon Area $m^2/g.$	Water Area $m^2/g.$	Calc. No. Water Layers	Activation Time Hr.	Activation Temp. °C.
0.55	4.35	7.9	24	25
0.68	1.33	2.0	1.0	350
0.91	0.87	0.9	3.0	400

The results for the adsorption of water on two samples of molybdenum, which were soxhleted with alcohol before use, are tabulated in the last two rows of Table I. Though the samples differed appreciably in area, both sorbed the equivalent of four layers of water with an average heat of wetting of 1,300 ergs/cm^2 per layer of water. These values seem high since, presumably, the bulk of the surface oxide film was removed. The weight loss of a sample of the larger area material after soxhleting to remove the oxide layer was determined to be 1.03% of the total weight of powder used. The calculated weight loss due to the removal of oxygen and water from this oxide film by reduction was calculated to be 0.64% assuming the oxide formula to be $MoO_2 \cdot 4MoO_3 \cdot 4H_2O$. The weight loss found experimentally after reduction of a second sample of this material

amounted to 0.62%. This direct evidence supports the contention that most of the oxide film was removed by soxhleting. However, the reduced sample only physically adsorbed water on its surface, whereas the soxhleted powder sorbed the equivalent of four layers of water, and so strongly that it could only be removed by high temperature activation. It appears, then, that all the surface oxide on molybdenum is removed by treatment with alcohol with the exception of a thin, perhaps monomolecular, hydrous oxide film. The average heat of hydration per mole of water sorbed on this film was found to be 24,900 calories.

Oxide Films on Molybdenum. - The data concerning oxide films on molybdenum reported here and in previous publications[2,10] are shown

(10) A. C. Zettlemoyer, J. J. Chessick and F. H. Healey, Heterogeneity of Surfaces, Adsorption of Gases on Metals, Technical Report No. 4, Office of Naval Research, June 1952. On file at the Library of Congress, Washington, D. C.

diagramatically in Figure 2.

The oxidation of molybdenum metal with dry oxygen at 25° produces a non-hydrous, monomolecular oxide film (I) with the probable formula MoO_2.[10]

The oxidation of molybdenum metal with moist oxygen at 25° yield a polymolecular, hydrous oxide film (II) of molybdenum blue $MoO_2 \cdot 4\ MoO_3 \cdot 4H_2O$. This film forms naturally on molybdenum powders stored at room temperatures in the presence of moist air.

Extraction with alcohol of molybdenum containing a surface film of "molybdenum blue" removes all the oxide except the hydrous layer adjacent to surface molybdenum atoms.

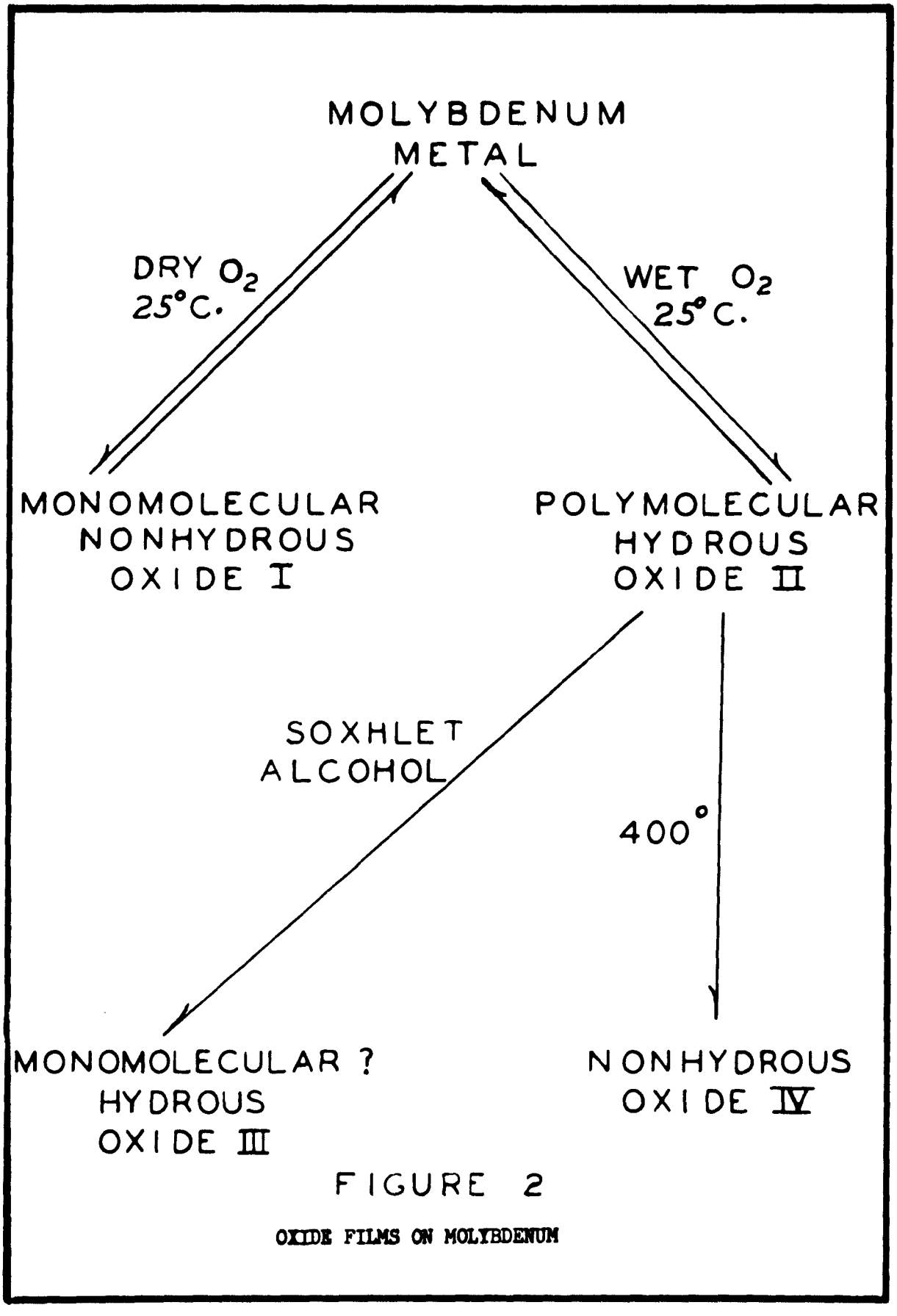


FIGURE 2

OXIDE FILMS ON MOLYBDENUM

A "molybdenum blue" film is transformed into a non-porous, chemically different oxide by high temperature activation. The composition of this oxide is not known.

Acknowledgment. - This work was carried out under contract N8onr-74300 with the Office of Naval Research whose support is gratefully acknowledged. The authors wish to thank Miss Yung-fang Yu for assistance in obtaining some of the adsorption data.

THERMODYNAMICS OF THE ADSORPTION OF WATER ON GRAPHON FROM HEATS OF IMMERSION AND ADSORPTION DATA

INTRODUCTION

The adsorption of water on Graphon has been previously measured by Pierce and Smith[1,2] and their results present several interesting

(1) Conway Pierce and R. Nelson Smith, J. Phys. and Colloid Chem. 54, 784 (1950).

(2) Conway Pierce and R. Nelson Smith, J. Phys. and Colloid Chem. 54, 795 (1950).

features. Graphon appears to be a surface which while generally considered homogeneous does possess a small fraction of heterogeneous sites. These sites have been considered[1] to be primarily responsible for the adsorption of water at low relative pressures.

In view of the very small amount of water adsorbed by Graphon at pressures below saturation, thermodynamic quantities cannot be calculated with any precision by the usual method of measuring adsorption isotherms at two temperatures. However, by combining the adsorption data with measurements of the heat of immersion of Graphon in water it has been possible to calculate both the absolute entropies of the adsorbed film and the isosteric heats of adsorption. The latter values represent the first such calculations made from heat of immersion data.

EXPERIMENTAL

Water vapor adsorption isotherms were determined at temperatures of 10° and 25° for Graphon[3]. This non-porous, graphitized carbon black

(3) We wish to thank Dr. Walter Smith of the Godfrey L. Cabot Company, Boston, Mass. for furnishing the Graphon, L-2739 and Mr. William Shaefer for his sincere attention to our numerous requests during the course of this investigation.

has an area as determined by nitrogen adsorption of about 83 m^2/g. The sample was degassed at 400° for 12 hours at 10^{-5}mm. before use. The samples were not treated with hydrogen since it was desired to preserve any heterogeneous sites on the surface.

The amount of water adsorbed was determined volumetrically using a modified Orr apparatus previously described[4]. Equilibrium pressures

(4) A. C. Zettlemoyer, G. J. Young, J. J. Chessick and F. H. Healey, To be published in the Journal of Physical Chem., October 1953.

were read after one hour on a manometer filled with Apiezon "B" oil. To check the extent of water absorption by the oil, adsorption isotherms were also determined using a mercury manometer. In these instances, time intervals as long as 24 hrs. were allowed before equilibrium pressures were read. No significant differences were found in the isotherms obtained by the two methods.

The calorimeter used in the heat of immersion studies has been described[4]. Values for the heat of wetting were obtained for evacuated Graphon and for Graphon coated with various amounts of adsorbed water. The film-coated Graphon was prepared on the adsorption apparatus and

sealed off at the desired equilibrium pressure. Care was taken to insure that the temperature of the sample was not altered during the sealing off process.

Two to three gram samples were used in the heat of immersion studies. Samples were used only once since it was found that the heat values obtained for a single sample in a series of runs increased slightly. This increase apparently does not result from a cleanup of the surface of Graphon by water, but rather from more profound changes, probably by limited surface oxidation in the presence of moisture. This explanation appears likely because the heat values for samples used only once were found to be the same whether these samples were activated at 25° for 24 hrs. or at 400° for 4 hrs.

Reliable isosteric heat data could not be obtained in the conventional manner because of the small amounts of water adsorbed over a wide pressure range. Approximate isosteric heat data obtained from adsorption isotherms at two temperatures did indicate that the values were below the heat of liquefaction of water.

RESULTS AND DISCUSSION

The isotherm for the adsorption of water on Graphon shown in Figure 1 has predominant Type III character, despite the slight rise in the curve at low pressures. At a relative pressure of about 0.95 only about 1/30 of a statistical monolayer of water was adsorbed. Pierce and Smith[2] who studied the adsorption of water on a similar carbon adsorbent which had been treated with hydrogen at 1100°C. reported that a relative pressure of about 0.99 was required to form one statistical monolayer;

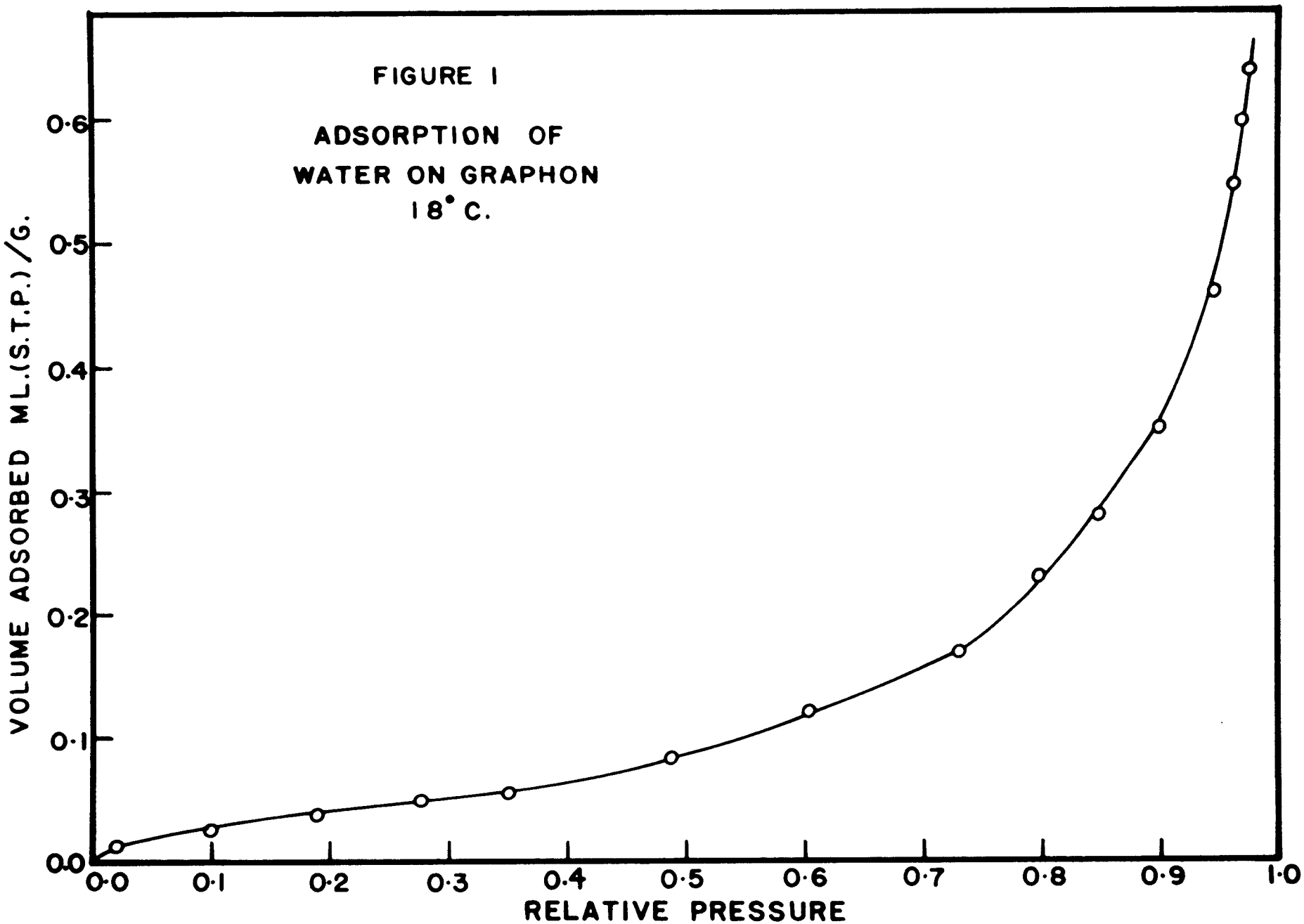


FIGURE 1
ADSORPTION OF
WATER ON GRAPHON
18° C.
VOLUME ADSORBED ML.(S.T.P.)/G.
0·0
0·1
0·2
0·3
0·4
0·5
0·6
0·0
0·1
0·2
0·3
0·4
0·5
0·6
0·7
0·8
0·9
1·0
RELATIVE PRESSURE

two statistical monolayers were adsorbed at 0.997. Further, these workers concluded that their isotherms at 0° and 28.6° were identical up to about 0.93. Experimentally it was found for the samples used in this study of the same relative pressure range that slightly greater amounts of water were adsorbed at the higher temperature.

Values for the heats of immersion of Graphon in water are shown plotted in Figure 2 as a function of the relative pressure to which the Graphon had been previously exposed. The curve differs markedly from the few curves for similar functions reported in the literature[4,5].

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(5) W. D. Harkins and G. Jura, J. Am. Chem. Soc., 66, 922 (1944).

These latter curves were obtained for the immersion of hydrophilic solids on whose surfaces duplex films of water form at saturation. The heat curves for these hydrophilic materials are characterized by high values at low surface coverages, and decrease rapidly to and remain near 118 ergs/cm^2; i.e., the heat liberated when one square cm. of a water-air interface is destroyed at 25°. In sharp contrast, the heat values found for the water-Graphon system are about 32 ergs/cm^2 near zero coverages and remain near this low value for samples exposed to water vapor over a wide range of relative pressures. Only at values of $x = 0.95$ do the heat values increase significantly. The shape of the heat of immersion curve is not unexpected. The hydrophobic graphon surface does not adsorb any appreciable amounts except near saturation pressure.

The isosteric heat values calculated from calorimetric data and an isotherm at one temperature are shown plotted as a function of volume adsorbed in Figure 3. The heat values lie below the heat of liquefaction in agreement with the approximate isothermal data at two temperatures.

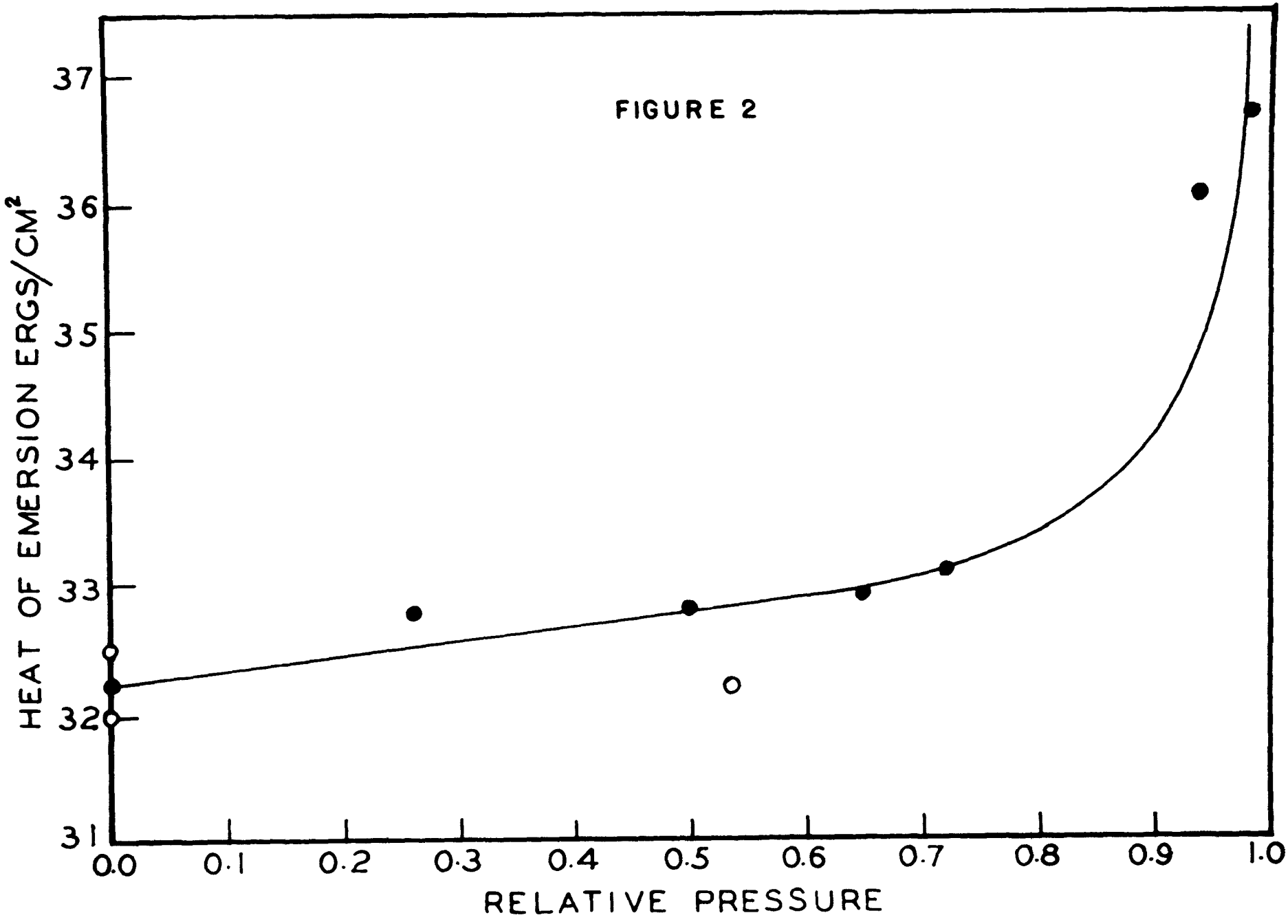
FIGURE 2
HEAT OF EMERSION ERGS/CM²
37
36
35
34
33
32
31
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
RELATIVE PRESSURE

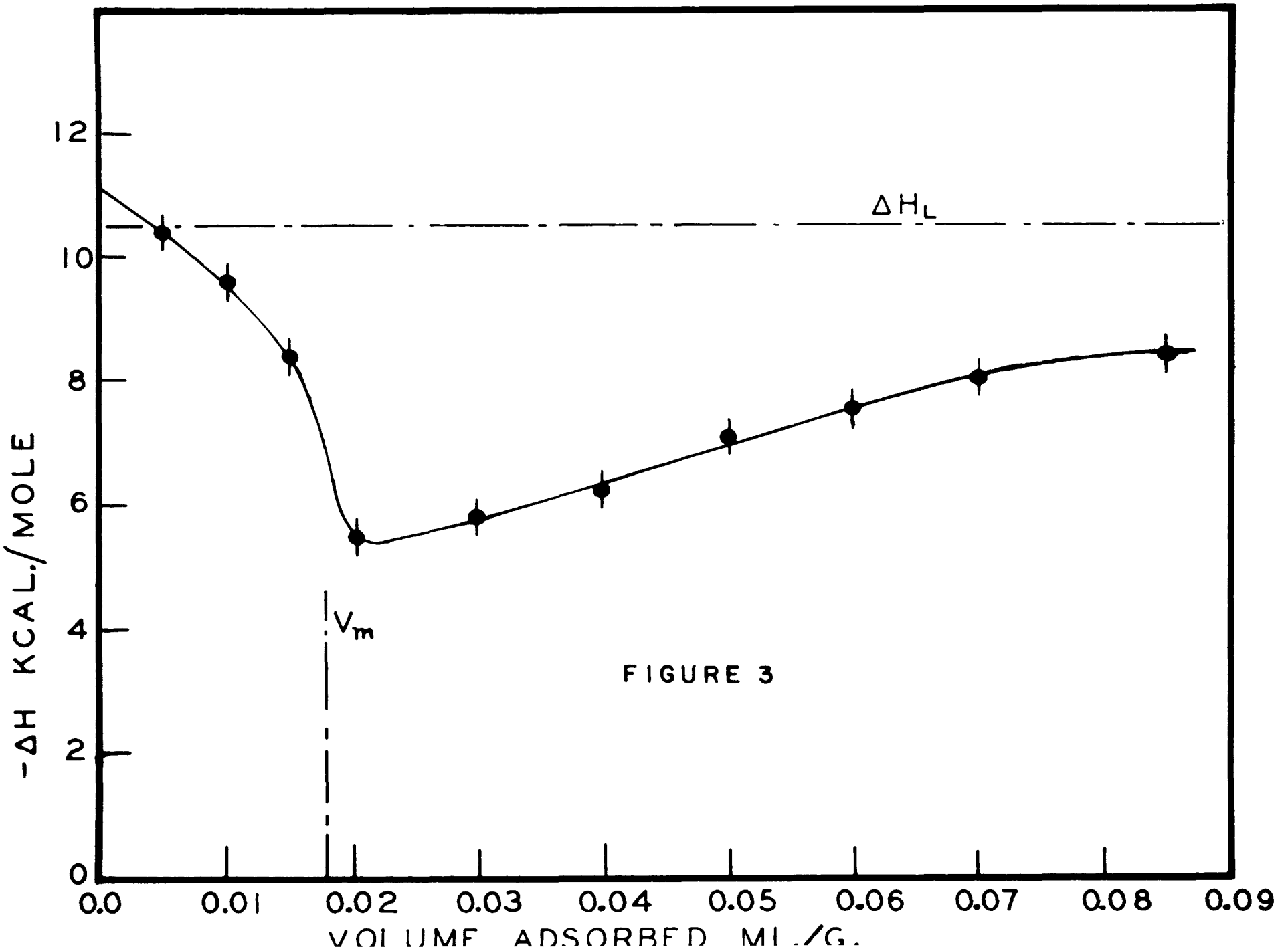
12
10
8
6
4
2
0
-ΔH KCAL./MOLE
ΔH_L
V_m
0.0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
0.09
VOLUME ADSORBED ML./G.

FIGURE 3

These results represent the first instance of the calculation of isosteric heat data from a combination of heat of immersion and adsorption isotherm data. The difference in the internal energy E_L, per mole of liquid adsorbate in equilibrium with vapor at T, and the energy, E_S, per mole of adsorbed molecules is given by the relationship[6]

$$(U_o - U)/N_S = E_L - E_S \qquad (6)$$

(6) G. Jura and T. L. Hill, J. Am. Chem. Soc., 74, 1498 (1952).

where $U_o - U$ is the difference in the heat of immersion of the clean solid and a solid with N_S adsorbed molecules. The energy difference $E_L - E_S$ is related to the isosteric heat, q_{st}, by an equation readily obtained from Equation 91 of Hill[7]

(7) T. L. Hill, J. Chem. Phys., 17, 520 (1949).

$$E_L - E_S = 1/N_S \int_0^{N_S} q_{st}\, dN_S - \Delta H_v \qquad (7)$$

where ΔH_v is the molar heat of vaporization of water. The isosteric heat is thus obtained by a graphical differentiation of an N_S $(E_L - E_S)$ vs. N_S plot. The calculated heat values are largely below the heat of liquefaction of water and pass through a minimum, near the calculated BET V_m value. The heat values then increase slowly toward the heat of liquefaction. The shape of the heat curve is strikingly similar to the curve for the adsorption of water on molybdenum sulfide which was recently reported by

Ballou and Ross[8].

(8) E. V. Ballou and Sydney Ross, Preprints of Paper, J. Phys. Chem., 27th National Colloid Symposium, June 25-27, 1953; p. 47.

The entropy of the adsorbed molecules, S_S, assuming an unperturbed adsorbent, was calculated from the equation

$$T(S_S - S_L) = \frac{U - U_0}{N_S} + \frac{\varphi}{\Gamma} - k\,T \ln x$$

as developed by Jura and Hill[6]. In this equation S_L refers to the entropy of the liquid, φ is the spreading pressure, Γ the surface concentration, and x the relative equilibrium pressure of the film coated solid. The entropy values shown in Figure 4 are essentially constant over the entire range of relative pressure studied.

The differential entropy $\bar{S}_S$ was obtained directly from the isosteric heat values using the expression

$$\bar{S}_S = S_G - \Delta S = S_G - \frac{q_{st}}{T}$$

where S_G is the absolute entropy of gaseous water at T and p.

The plots of S_S and $\bar{S}_S$ as a function of the volume of water adsorbed are shown in Figure 4. Both curves exhibit a minimum and maximum and it is to be noted that the curves intersect at the maximum and minimum of the S_S curve. These intersections follow as a mathematical consequence of the relation between the two quantities, but inasmuch as different methods of calculation were used for S_S and $\bar{S}_S$ the correct intersection provides a check on the computations.

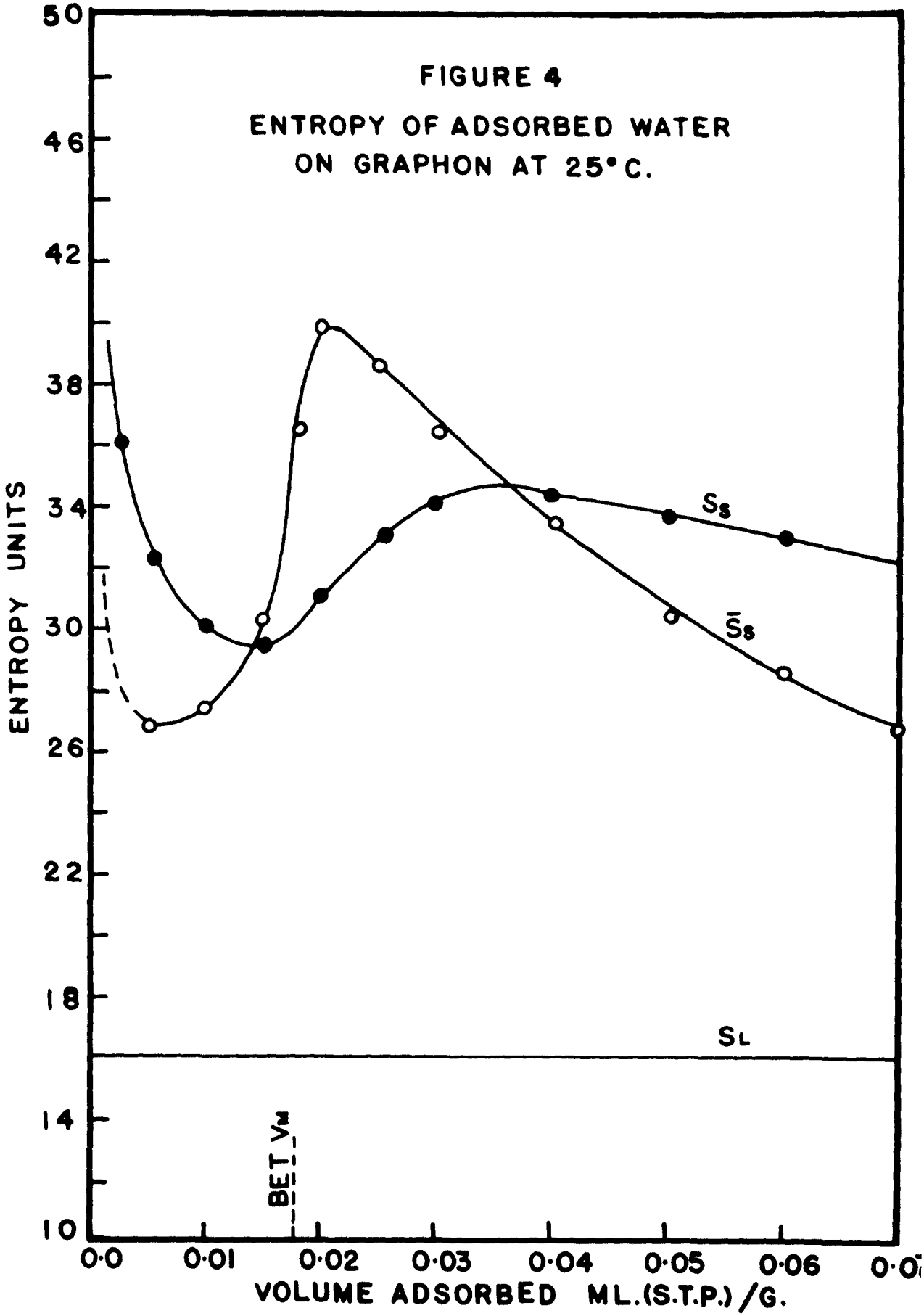
FIGURE 4
ENTROPY OF ADSORBED WATER
ON GRAPHON AT 25°C.
ENTROPY UNITS
50
46
42
38
34
30
26
22
18
14
10
S_s
$\bar{S}_s$
S_L
BET V_M
0·0
0·01
0·02
0·03
0·04
0·05
0·06
VOLUME ADSORBED ML.(S.T.P.)/G.

The minimum in the S_g curve has been taken[9] as a thermodynamic

(9) T. L. Hill, P. H. Emmett and L. G. Joyner, J. Am. Chem. Soc., 73, 5105 (1951).

criterion for the completion of the first layer of adsorbed molecules, i.e., $V = V_m$. This minimum S_g for water on Graphon is seen in Figure 4 to be in excellent agreement with the value for V_m calculated from the BET equation. This close correspondence is worthy of special note since the amount of water adsorbed at the BET V_m amounts to only about 1/1500 of the value that would be expected from the nitrogen surface area. Thus, these two entirely independent approaches indicate that the adsorbed water molecules begin to build up in a second layer when only a very small fraction of the surface has been covered.

It is apparent that such behavior can only be explained on the basis of at least two types of adsorption sites on the Graphon surface. The vast majority of the surface sites are hydrophobic and must correspond to the graphite-like array of carbon atoms. These sites show no tendency to adsorb water, at least up to pressures close to saturation. The hydrophilic sites are few in number and probably arise from traces of surface oxide such as might be expected to form at the edge atoms of the graphite planes. It would be these sites that would account for the initial Type II character of the water adsorption isotherm. These sites are probably of unequal energies as shown by the decrease in the isosteric heat below V_m (Fig. 3) but as a group are still vastly different from the remainder of the surface. After the adsorption of the first layer of water molecules on these sites the molecules build up additional layers on and around these sites rather than adsorb on the adjacent hydrophobic area.

The concept of the cluster-wise adsorption of water on graphon has also been used by Pierce and Smith[1] to explain the hysteresis loop found in the isotherm at high relative pressures.

It may be surprising that the heat of adsorption on almost all of the hydrophilic sites is well below the heat of liquefaction. However, it must be remembered that the high heat of liquefaction of water is due largely to the formation of hydrogen bonds and that when no such bonding can take place in the adsorption process it is reasonable for the heat evolved to be considerably less. Indeed, a second molecule going down on top of the single adsorbed molecule should still have less opportunity for interaction than in the liquid. The heat of adsorption thus rises only gradually toward the heat of liquefaction.

For the same reasons the entropy of the adsorbed water molecules is not as low as in liquid water. Inasmuch as the shape of the isosteric heat curve indicates that energies of these sites are not the same, it does not appear possible to account for the high entropy values by including a configuration entropy term for the ways in which the molecules could distribute themselves among the sites. If the sites are all of different energies there can only be one equilibrium distribution of identical molecules at a given pressure.

The surface of Graphon is generally considered[10] to be quite uniform. The present results do not, of course, contradict this conclusion

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(10) R. A. Beebe, J. Biscoe, W. R. Smith and C. B. Wendell, J. Am. Chem. Soc. 69, 95 (1947).

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since the heterogeneity reported here concerns only about 1/1500 of the surface. For adsorbents such as argon and nitrogen the effect of this

minute fraction of the surface would be obscured even if the adsorption energies were quite different on the two types of surface sites. Nevertheless, the small amount of heterogeneity may be a critical factor in the observed properties of the material. It has been well demonstrated by Savage[11] that the wear properties and lubricating action of graphite are

(11) R. H. Savage, Ann. N. Y. Acad. Sci. 53, 862 (1951).

greatly improved by the presence of water vapor even at low pressures. Since both graphite and Graphon have similar crystalline arrays of carbon atoms, the water adsorption on graphite must also mainly occur on the hydrophilic oxide and impurity sites. It is indeed striking that, though little of the surface is covered by adsorbed water molecules, the presence of these few molecules is sufficient to prevent the rapid wear of carbon brushes in electric motors, and to allow the use of graphite as a lubricant.

WORK NOW IN PROGRESS

The investigation of surface heterogeneity in this Laboratory has to date demonstrated that a metallic surface may have both a real physical heterogeneity due to surface irregularities and an apparent chemical heterogeneity due to changes in the work function of the metal during the adsorption process. Both of these types are important to an understanding of the behavior of molybdenum toward oxygen at low temperatures. The studies of Graphon by adsorption and heat of immersion techniques illustrated the importance of active sites even when they are only sparsely distributed on the surface. Calculation of thermodynamic quantities relating to the adsorption process have proved of great value in characterizing the heterogeneous nature of the surfaces studied.

A summary of current work undertaken in the period following that covered in the previous sections of this report is as follows:

1. Heats of immersion measurements for a series of normal hydrocarbons and alcohols have been obtained for Graphon. The purpose of determining the heats of wetting of these materials was to observe the relative importance of non-polar van der Waal's forces in adhesion binding as the chain length and polarizability of the adsorbed molecules changes. Graphon provides a useful surface for this study since its almost completely homogeneous surface will allow a ready comparison of adsorbate interactions. Further studies will include heats of immersion in other organic molecules such as ethers, acids and branched chain compounds.

2. To supplement the studies of non-polar gas adsorption a low temperature calorimeter operated at -195°C. has been designed and

preliminary measurements of the heats of immersion of magnesia and graphon in liquid nitrogen have been made. The heat values found were approximately 105 ergs/cm^2 for both materials. The heat evolved is determined in a simple manner from the volume of gas evolved when a clean sample is broken under liquid nitrogen.

3. Isotherms for the adsorption of argon on reduced molybdenum powder are being determined at a series of temperatures. The change in the surface heterogeneity of this metal are to be studied as a function of sintering caused by high temperature reductions. Similar studies with other metals are planned.

4. A controlled step-wise exidation of a Graphon surface is planned in order to study the influence of heterogeneity on the adsorption characteristics of this material with regard to its behavior toward water.

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